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Electrode material enhancements for lead-acid batteries

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ABSTRACT

Exide Technologies has received a contract from TARDEC to develop a 4HN format battery with AGM separator technology. In addition to redesigning the current flooded battery to use Absorbed Glass Mat separator, the battery will be the test vehicle for materials research aimed at improving battery performance. The effort is split into two main topics: ceramic additives for positive and carbon additives for negative active materials.

1. INTRODUCTION

While Lithium-ion technology has received the majority of research interest in recent years, significant work has taken place to improve lead-acid systems, which represent one of the world's most used batteries. Exide Technologies has been involved in research to improve the electrode materials which have been in use for over a century. Both positive and negative electrode materials are believed to be candidates for the use of additives to improve the performance of the battery.

2. DISCUSSION

2.1. Carbon Additive in Negative active materials

Carbon has been the favored additive to the negative active material (NAM) of lead-acid batteries to mitigate the growth of lead sulphate for several decades. Even though there has been no consensus on mechanism or role of carbon in NAM, several beneficial effects are known. Carbon nucleates the PbSO₄ crystals resulting in smaller crystals which could be dissolved back into the electrolyte during charging process. This restricts the progress of plate sulfation which increases the useful life of the battery in high rate partial state of charge cycling duty. High surface area carbons act as a reservoir for electrolyte within NAM thus reducing the possibility of plate dry out.

Exide's existing flat plate advanced glass mat (AGM) batteries comparable to 4HN type battery with high carbon

batteries were built in one of Exide Technologies' manufacturing facility. Standard batteries with no additional carbon, 3 wt % and 6 wt% carbon loadings were used. The carbon formulation consists of a mixture of Graphite and Carbon black materials. The negative plates were pasted to current specification thickness instead of maintaining plate weight constant due to decrease in plate density with carbon addition. The paste densities reduced by .80 to .90 g/ while negative active material weights reduced by 24% - 31% with the addition of 3 and 6 wt % carbons.

Initial characterization of the batteries included static charge acceptance test performed at 0 °C, 50% depth of discharge (DoD), dynamic charge acceptance test performed at 60 – 90 % state of charges (SoC). The discharge capacities include discharge at C/20 rate (low rate), reserve capacity (mid rate) and cold cranking amps (CCA - high rate).

Carbon enhanced negatives with carbon and graphite mix yield an increased charge acceptance capability on the order of 2X (Figure 1). No significant difference was observed between 3 wt% and 6 wt% carbon loadings. For applications where increased charge acceptance is a benefit, carbon additives can be an ideal solution. When the batteries were tested further at various states of charges, similar trend was observed. An increased charge acceptance with Carbon was noted with increasing depth of discharges (Figure 2).

Carbon batteries at 3 wt% loading showed little variation at low rate (C20) and mid-rate (RC) discharges while

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batteries with 6 wt% loading showed a negative impact on the capacities (Table 1). While this decrease is noteworthy they can be engineered around to minimize impact. The cold cranking ampere test was performed using a two discharge steps – 925 Amps (rated CCA) for 10 seconds followed by a 30 seconds rest and 555 Amps (60% of rated CCA). A significant negative impact on high rate capacity was noticed for both 3 and 6 wt % carbon batteries (Figure 3).

Carbon enhanced negatives with carbon and graphite mix yield an increased charge acceptance capability on the order of 2X. Low rate (C20) and mid-rate (RC) can be negatively effected but can be engineered around to minimize impact. A significant negative impact on high rate capacity (CCA) was observed for carbon batteries. Future studies from this part of work includes optimization of carbon loading for highest performance improvement, and cycle life test on 3 And 6 wt% carbon samples.

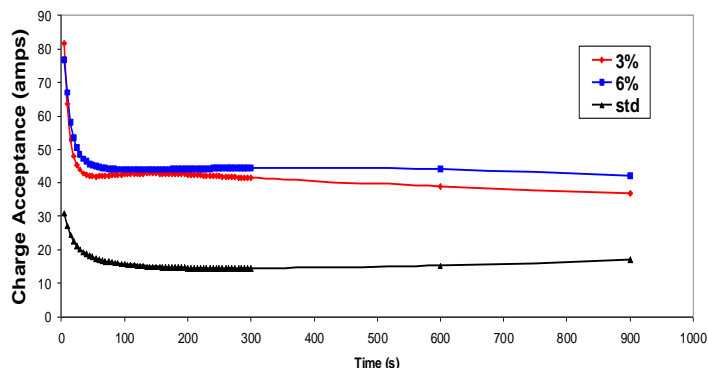


Figure 1. Static charge acceptance for standard, 3 wt% and 6 wt% carbon samples measured at 0 °C, 50% depth of discharge (DoD).

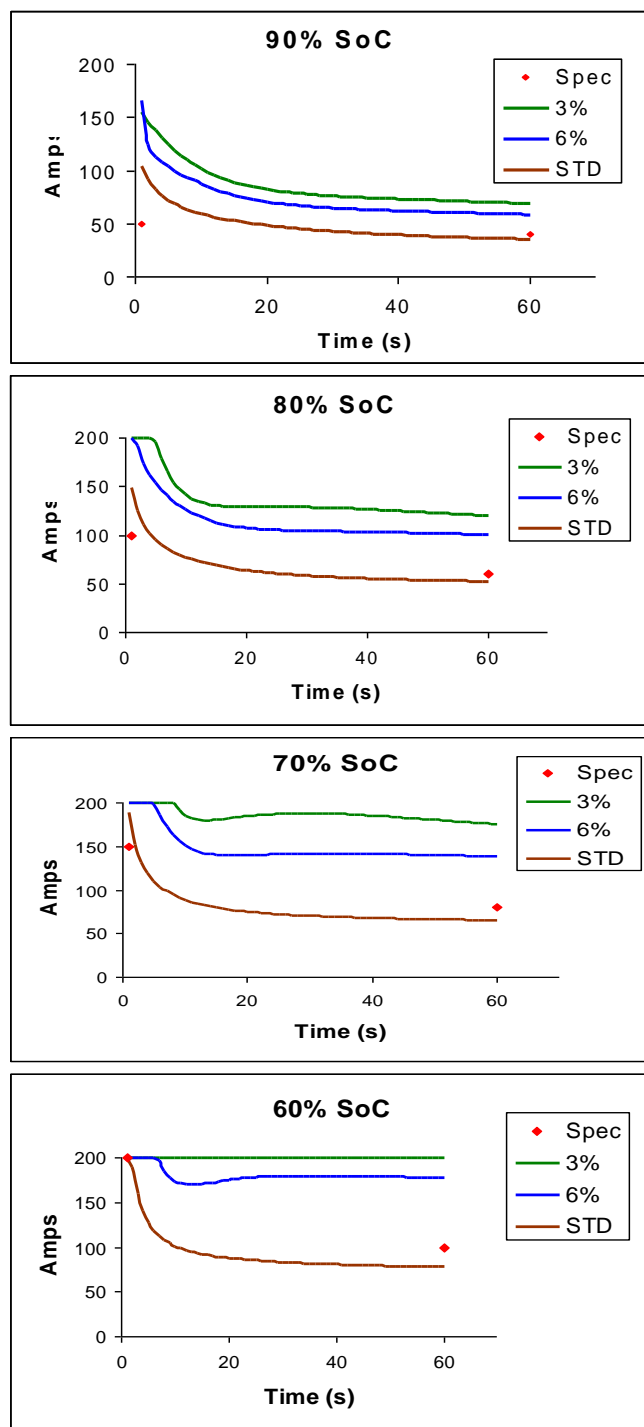


Figure 2. Dynamic charge acceptance for standard, 3 wt% and 6 wt% carbon samples measured at 0 °C, 60 - 90% depth of discharges (DoD).

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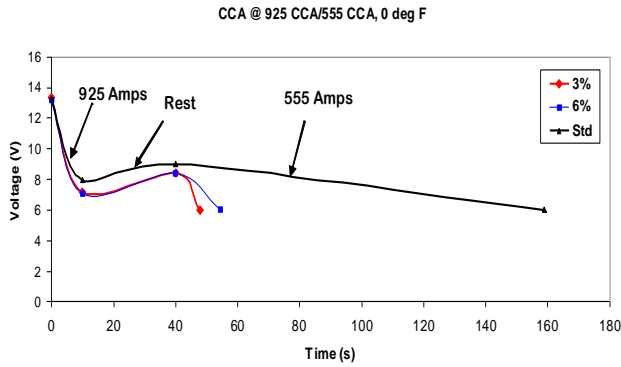


Figure 3. Cold cranking amperes for standard, 3 wt% and 6 wt% carbon samples measured at 0 F. Two discharge steps were used – 925 Amps (rated CCA) for 10 seconds followed by a 30 seconds rest and 555 Amps (60% of rated CCA).

Table 1. Low and mid rate capacity effect for the standard, 3 wt% and 6 wt% carbon samples

Variable	C20 (Ah)	C20 (% impact)	RC(min)	RC (% impact)
Std	105.03	-	220.36	-
3.0%	107.24	2.1%	221.46	0.5%
6.0%	82.06	-21.9%	172.98	-21.5%

2.2 Positive active material enhancement

Trials of batteries made in our 2" by 3" reference battery are being completed. The current work examines control cells and cells made with 5% and 10% conductive additive by weight. All of the positive plates were made on the same day and cured simultaneously to minimize variation in paste performance due to oxide variation. The negatives were all made on the next day and cured separately from the positives.

Tests of capacity and power were performed on available 25A circuits on all cells. The results shown below show statistically significant improvement of the overall cell in providing power and statistically significant improvement in capacity as different discharge rates. Unless noted, the values shown are not corrected for mass of the cell or for the amount of paste present in the positive grids. The cells are assumed to be positive limited, give the 2 positive/3 negative grid configuration.

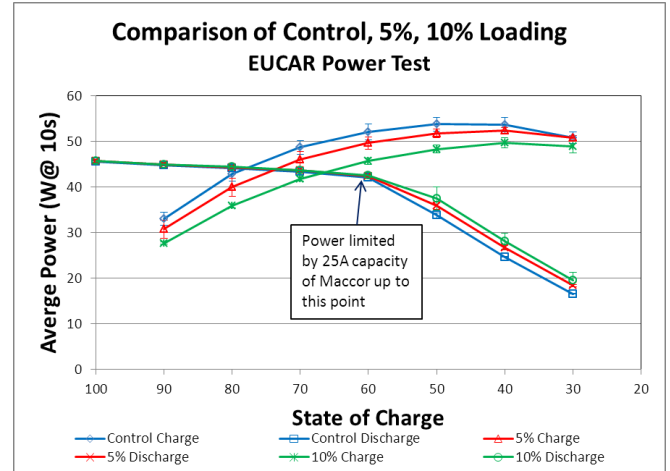


Figure 1 EUCAR power test with un-normalized data

The discharge and charge pulses of the EUCAR power test reached the 25A limit of the available testing circuits until the cells dropped below 50% state of charge. Even then, an increase in discharge power is seen even without normalizing for initial cell weight. The lines shown represent the average of three cells with vertical error bars showing the standard deviation of the cells. The discharge curves are the reverse of the expected order, but normalizing for weight of PbO in the positive grids reverses this trend. As shown below.

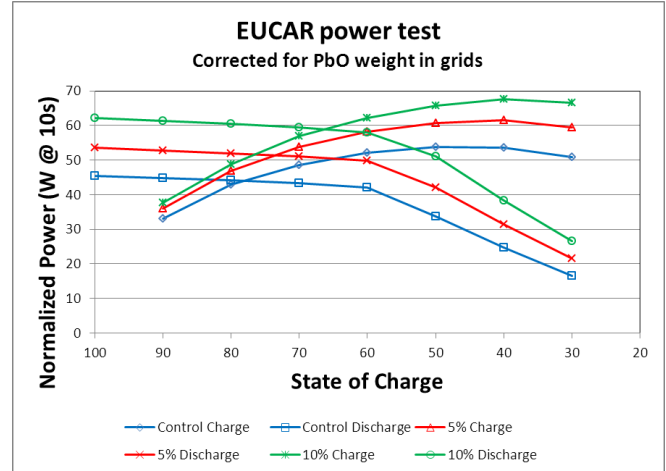


Figure 2 EUCAR power tests corrected for weight of PbO in positive grids

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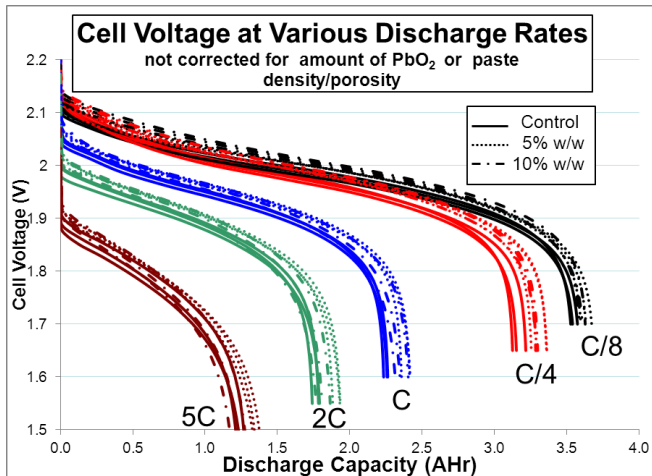


Figure 3 Discharge curves at C/8, C/4, C, 2C, and 5C rates. Not corrected for positive paste weight

The graphs of various rate discharges show an improvement in capacity of the 2" by 3" cells with the presence of the conductive ceramic additive. The graphs in Figure 3 are not corrected for differences in paste density or porosity. Even with these "black box" measurements there is a significant improvement in the capacity of cells with additives even at the higher discharge rates. Once normalized by the amount of PbO per plate in the positive the trend in improvement is easier to see, Figure 4.

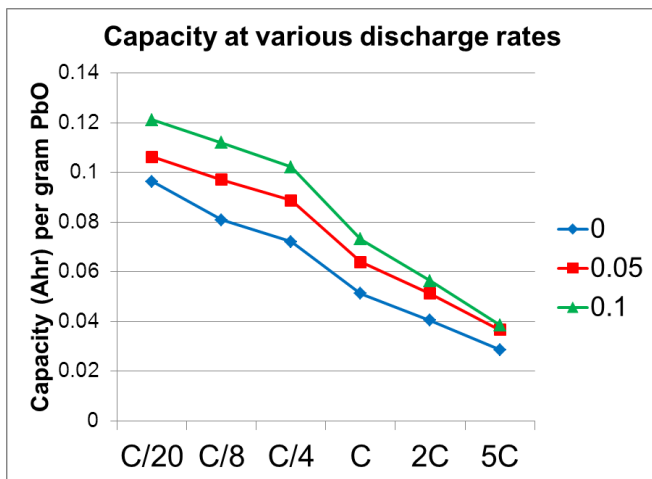


Figure 4 Capacity per gram of PbO in positive active material

Ongoing work is focusing on optimizing additive level and also paste density and porosity to maximize the power of the cells. Additionally, after re-testing the created cells on higher amperage circuits, they will start cycle life testing.

3. Conclusion

Exide Technologies' work towards improving the performance of lead-acid battery electrodes is showing positive results. Further testing involving the effect of additives on cycle life is planned.

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